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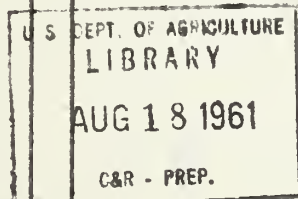


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X HEAT-, MILDEW-, AND ROT-RESISTANT COTTONS ;  
X Acetylated or Cyanoethylated X

Southern Utilization Research  
And Development Division  
New Orleans, Louisiana  
Sec 7 //



Compiled by  
Marie A. Jones  
March 1961  
SC //

Agricultural Research Service .  
U. S. Department of Agriculture



MAKING COTTON RESISTANT TO HEAT, MILDEW, AND ROT

As part of a general program to transform cotton into new and improved products by means of chemical modification, a great deal of work has been done by Southern Division scientists on acetylation and cyanoethylation. Both of these treatments impart improved resistance to heat, and to deterioration from mildew and rot. This is also true of various other treatments being investigated by researchers at the Southern Division and in other organizations. Among the most promising processes developed here for this purpose are those employing the acid colloids of methylolmelamine, and tris(1-aziridinyl) phosphine oxide (APO). Both of these compounds when applied in a suitable manner, and to the required add-on, give excellent resistance to mildew and rot, but are susceptible to scorching when subjected to high temperatures.

Processes based on those developed at the Southern Division are the first to be used commercially in the United States. Applications based on the heat and rot resistance of PA cotton were developed first by this Division. However, the processes of partial acetylation did not originate here. British scientists made the first reports of a fibrous partially acetylated cotton yarn in 1901, and an acid-catalyzed process for producing it was patented in 1933. Another British product, described in earlier patent specifications as being produced by a zinc chloride-catalyzed process, is called Cotopa (or Crestol, if applied to mercerized cotton). These products have been made in Great Britain for a number of years.

Both acetylated and cyanoethylated cottons are distinguished by their high degree of resistance to heat damage and scorching. PA cotton was commercialized in this country in 1953, and is now being manufactured by one firm for use in home ironing board covers. This product enables cotton to compete with asbestos for this purpose. It also has excellent possibilities for the commercial laundry industry and has proved in actual service trials in commercial laundries that it will last five or six times as long as untreated fabric. Based on the assumption that PA cotton can displace 50% of the competing materials in the commercial laundry field, potential increase as a result of this development is estimated at 9,000-17,000 bales of cotton annually (worth from \$1.5 to \$3 million).

Besides being resistant to heat, PA cotton resists deterioration from mildew and rot. One of the first uses suggested by this property was for sandbags. Interest in a number of other possible uses has been expressed recently by various commercial manufacturers, for example, in belting, plastic laminates, shoe tops and liners, felting material for floor coverings, insulation of hot pipes, and in construction of sand fences.

Cyanoethylated (CN) cotton has several properties similar to those of PA cotton, such as heat, mildew, and rot resistance. Both PA and CN cottons, are thermoplastic, when reacted to a sufficient degree of substitution, a property which adds to their potentialities as there is considerable interest in thermoplastic cotton fabrics both here and abroad.

Interest in cyanoethylated cotton has been stimulated recently because of increased production of acrylonitrile, which is employed in the treatment, and because of the development of improved processing methods. CN cotton accepts direct dyes less easily than does native cotton, but takes acid and acetate dyes more readily. Flat abrasion resistance is greater than untreated cotton, while flex abrasion is less. The CN cotton also has improved electrical properties which make it of interest as an insulation material.

A number of papers describing research on CN cotton have been published by the Institute of Textile Technology. A review of research in this field, "The Cyanoethylation of Cotton in Aqueous Medium," (by N. M. Bikales and L. Rapoport, *Textile Recorder* 58, 936, 71-74, 1961) gives an extensive list of references to published papers on the subject.



## PREFACE

An abstract bibliography of all publications reporting research by the Southern Utilization Research and Development Division on the utilization of cotton is now being prepared. For the convenience of those who may be interested in a specific area of work, however, we have also prepared listings of publications on research in some special fields.

Because of the interest in acetylation and cyanoethylation of cotton fabrics, we are presenting in this booklet abstracts of our publications and patents on our investigations in this area. Also included in this listing are some papers on the treatment of cotton with acrylonitrile in the presence of gamma radiation.

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PUBLICATIONS PLANNED**THE VAPOR PHASE CYANOETHYLATION OF COTTON**

Janssen, Hermann J., Steen, Gary J., Haydel, Chester N.,  
Vix, Henry L. E.; and Gastrock, Edward A.

The relative quantities of cyanoethyl nitrogen and of a yellow-colored alkaline-catalyzed polymer nitrogen formed during the vapor phase cyanoethylation of cotton yarn with acrylonitrile has been determined under a variety of processing conditions. The use of reaction temperatures near 70°C., low wet-pickups of catalyst solution, low concentration of catalyst in solution and short reaction times were required to accentuate cyanoethylation and to minimize polymerization. Recommended polymerization inhibitors proved rather ineffective, although some benefit was derived from addition of nitric oxide to the reagent or of catechol to the catalyst solution. Infrared studies of the alkaline-catalyzed polyacrylonitrile indicated that the nitrile group had probably undergone partial hydrolysis with formation of carbamoyl. The breaking strength, elongation-at-break, and the heat-, acid-, and rot-resisting properties of the vapor phase cyanoethylated products proved comparable with those of cotton yarn cyanoethylated in the liquid phase to equal nitrogen content.

**HEAT AND SCORCH RESISTANT COTTON COVERS FOR HOT HEAD PRESSES**

Cooper, A. S., Jr., and \*Duckworth, Norman

The American Institute of Laundering, in cooperation with the National Cotton Council and the Southern Division, carried out limited service evaluation tests of partially acetylated and cyanoethylated cottons as covers for hot head presses. These tests indicate that cotton can be chemically modified so that it has heat and scorch resistance properties that are comparable to nylon on a use-quality and cost-performance basis when used as covering material for such presses.

**THE PREPARATION AND EVALUATION OF SELECTED FABRIC ESTERS OF COTTON**

Cruz-Lagrange, Manuel D.; Hamalainen, Carl; and Cooper, Albert S., Jr.

Eight different partial esters of cellulose in fabric form were prepared using trifluoroacetic anhydride impellent procedure having approximately the same acyl contents. Their physical properties were measured. It was found that with an increasing molecular weight of the ester group there was usually an attendant decrease in the retention of the specific property evaluated. An exception was in the wet wrinkle recovery. Some of the ester samples exhibited an appreciable degree of thermoplasticity in that sharp creases pressed into the fabric were retained through several launderings. This feature could be used to advantage in apparel applications such as in the formation of pleats and in shaping fabrics.

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\* American Institute of Laundering

## IMPROVING THE DIMENSIONAL STABILITY OF ACETYLATED COTTON PRODUCTS

Sloan, William G.; Tallant, John D.; and Hobart, Stanley R.

The dimensional stability of partially acetylated and fully acetylated yarns and fabrics has been improved by heat-stressing treatments which are described. Heat-stressing for as little as 30 seconds caused considerable reduction in elongation-at-break, a sharp increase in secant modulus, and more importantly considerable reduction in growth of permanent set after cyclic loading. Breaking strengths of the yarns and fabrics were not adversely affected by the heat-stressing treatment. Data are given for partially acetylated and fully acetylated yarns and fabrics after treatment at temperatures ranging from 100°C. to 245°C. and under loads up to 50% of breaking strength. Best results were achieved by heat-stressing for 30 seconds at 200°C. under a load equal to 20% of the breaking strength.

PUBLISHED PAPERS

## 2080. HOW TO MAKE PA COTTON

Sens, Charles L.; Sloan, William G.; and Cooper, Albert S., Jr.  
Textile Inds., 125 (3): 101, 105, 107, 109, 113, 115-16. 1961

Investigations were conducted to determine the optimum percentage of partially acetylated (PA) cotton to blend with untreated cotton for processing into yarns and fabrics. It was found necessary to use a blend of 70% PA and 30% untreated cottons to obtain relatively good heat resistance and mechanical processing. This blend was processed into a fabric for comparison with other fabrics produced from acetylated roving, acetylated yarn and acetylated fabric. These comparable fabrics were evaluated by physical property measurements before and after heating for various periods at 160°C. to determine at what stage of mechanical processing acetylation should be performed. On the basis of these simulated service tests, fabrics acetylated in fabric form or as yarn were slightly better than the fabric produced from acetylated roving, and considerably better than the fabric produced from a blend of acetylated and untreated cotton. While various techniques for acetylating raw stock, roving and yarn have been developed on a pilot-plant scale, fabric acetylation is still preferable from a commercial standpoint. However, many industrial fabrics are either too tightly woven or too wide for acetylation as piece goods. For these types of fabrics, acetylation in yarn form would be the preferred method of treatment.



## 2042. FA COTTON FABRIC: PRELIMINARY COST STUDY

McMillan, O. J., Jr.; Decossas, K. M.; Cooper, A. S., Jr.;  
Hamalainen, C.; Murphy, A. L.; and Pollard, E. F.  
Am. Dyestuff Repr. 49, 839-842. 1960

FA cotton, a chemically modified cotton in which acetyl groups are introduced into the cellulose molecule, has excellent electrical insulating properties, rot resistance, heat resistance, and flat abrasion resistance. This product may be prepared from cotton in raw stock, yarn, and fabric form. In this cost study we have considered cotton in only fabric form having a degree of substitution of 2.0, that is, an average of two of the three hydroxyl groups per anhydroglucose unit has been replaced by acetyl groups. Details of the process and hypothetical plants are described for producing this fabric produce in 500-yard batches using conventional textile processing equipment. Investment costs, operating costs, and general expenses are given for plants with annual capacities of from 125 thousand linear yards up to 2.1 million linear yards. It was determined in this cost study that at the present stage of process development, a fabric product, having a DS of 2.0, can be produced at a cost of 55.5¢ down to 28.3¢ per linear yard, or \$1.30 down to 66.3¢ per pound of product. Captive supply or contract purchasing of chemicals and future process improvements could probably reduce these costs by as much as one-third.

2016. HIGH ENERGY  $\gamma$ -IRRADIATION OF VINYL MONOMERS. II. INFRARED SPECTRA OF RADIATION-POLYMERIZED ACRYLONITRILE

Arthur, Jett C., Jr.; and Demint, Robert J.  
J. Phys. Chem. 64, 1332 (1960)

The sharp bands were: 3.4, 6.8, and 7.4  $\mu$ , -CH<sub>2</sub>; 4.5  $\mu$ , -CN; 8.0  $\mu$ , -CH; 9.3  $\mu$ , -C-CN. The change in structure of the radiation-polymerized acrylonitrile at higher dosages (ranging from 5.2 to 520 x 10<sup>21</sup> electron volts per liter from cobalt-60) was probably that resulting from a dehydrogenation followed by crosslinking between two or more polymeric molecules.

## 1984. PROPERTIES OF COTTON CONTAINING RADIATION-POLYMERIZED ACRYLONITRILE

Arthur, Jett C., Jr.; and Demint, Robert J.  
Textile Research J. 30, 505-509 (1960)

The modification of the physical properties of cotton fiber, by exposing the fibers in the presence of acrylonitrile monomer, has been accomplished. Relatively large quantities of acrylonitrile monomer in aqueous zinc chloride were applied to cotton and radiation polymerized in the presence of the cotton. Microscopic examination indicated that the polymer was located within the fiber. There was only a slight decrease in breaking

strength, a significant increase in elongation-at-break, and a decrease in stiffness of the fibers. Resistance to acid and to heat degradation of the yarn containing polyacrylonitrile was comparable to that of untreated yarn. A radiation dosage of 0.8 megarep gave a maximum add-on of polymer. The results are particularly interesting relative to the preparation of chemically modified cottons. Work will be continued to investigate the application of additional chemicals to cotton by high energy radiation and to evaluate the properties of these chemically modified cottons.

1951. CHANGES IN FINE STRUCTURE AND MECHANICAL PROPERTIES INDUCED BY CYANOETHYLATION OF COTTON YARNS. PART I: TREATED WITHOUT TENSION

Conrad, Carl M.; Stanonis, D. J.; Harbrink, Pieter; and Creely, J. J.

Textile Research J. 30, 339-348 (1960)

Cotton yarns were impregnated with 6% sodium hydroxide and reacted in the relaxed state with acrylonitrile at 60°C. and different periods of time up to 60 min. to give products with degrees of substitution up to 2.6 cyanoethyl groups per anhydroglucose unit. As substitution increases the x-ray diffraction pattern shows only slight alteration until substitution has exceeded 1.1, after which the crystalline structure rapidly gives way to an amorphous structure, complete at about  $DS = 2.0$ . At the same time density decreases nearly linearly with substitution. At the stage where the product becomes essentially amorphous, it can be annealed at temperatures of about 175°C. into a new pattern characteristic of cyanoethyl cellulose. This annealing is accompanied by a substantial density increase. Stress relaxation of the cyanoethylated yarns at a substitution of 1.1 suggests a glass-rubber transition point about 140°C. which becomes more distinct and moves to lower temperatures as substitution increases. At a substitution of about 2.0 the stress relaxation reaches its lowest value (about 4% of the value at 20°C.) at the highest temperatures tested (220°C.). With further substitution a minimum relaxation at an intermediate temperature is followed by increasing stress as the temperature is raised. This effect is associated with crystallization. Breaking strength increases slightly at low substitutions but decreases then to less than 50% for the highest substitutions. Elongation at break increases gradually, exceeding 100% above the control at  $DS = 2$  and above. Tensile stiffness decreases to about 3% of its initial value. Work of rupture and recovery show considerable decreases below  $DS = 2$ , but sharp rises between 2.0 and 2.6. Immediate elastic recovery is little affected below  $DS = 2$ , but rises above this. Delayed elastic recovery shows continuous improvement as substitution increases, eventually exceeding the control by nearly 50%.



1843. USE OF TRIFLUOROACETIC ANHYDRIDE IN PARTIAL ACETYLATION OF COTTON CELLULOSE

Hamalainen, Carl; Wade, Ricardo H.; and Cruz, Manuel D.  
Textile Research J. 29: 821-26. 1959

Trifluoroacetic anhydride (TFAA) has been found to be an effective esterification promoter in the preparation of experimental quantities of partial cellulose acetates in which the fibrous structure of the original cotton is retained. In this reaction TFAA acts as an impellent and no additional catalyst is required. A method of preparation has been devised, and the effects of time, temperature, and molar ratio of the components in the reaction system have been studied. Optimum reaction conditions are mild with no great degradative effects. Cotton in the form of yarn has been reacted, and the composition and physical characteristics of the modified yarns have been determined.

1837. RADIATION POLYMERIZATION OF ACRYLONITRILE ONTO COTTON

Arthur, Jett C., Jr.; Demint, Robert J.; McSherry, Wilbur F.; and Jurgens, Julian F.  
Textile Research J. 29: 759. 1959

In the course of investigations involving the determination of the effects of gamma radiation on cotton cellulose and on polymerization of vinyl monomers, a technique for the application, or possibly grafting, of large, controlled quantities of polyacrylonitrile onto cotton has been developed. Acrylonitrile monomer was uniformly applied to purified 7/3s yarn, Deltapine cotton, and then polymerized by gamma radiation from cobalt-60. The yarns were extracted overnight by N,N-dimethylformamide at 25°C. to remove any monomer and soluble or loosely bound polymer. Polymer contents, as high as 26%, were received.

1834. POTENTIAL MARKETS FOR PARTIALLY ACETYLATED COTTON

\*Barlow, Frank D., Jr.; Cooper, Albert S., Jr.; and Vix, Henry L. E.  
USDA Publication, AMS-324: 22 pages. 1959

Improved properties resulting from partial acetylation of cotton are resistance to rot, mildew, heat, and scorch. The opportunity for commercializing PA cotton, from a cost standpoint, is confined primarily to utilizing the properties of scorch and heat resistance, important properties for commercial laundry textiles and home ironing board covers. Service evaluations in which

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\*Market Development Branch, Agricultural Marketing Service.

fabrics were exposed to sustained temperatures of 300°F. or more indicated that the service life of PA cotton was about 4 times that of untreated cotton. The estimated costs of PA cotton based on pilot plant and commercial operation, further provided a basis for assuming a favorable competitive position for PA cotton versus untreated cotton and other materials used in commercial laundry textiles. Based on the National Cotton Council's 1956 statistics for cotton consumed in the laundry industry and cotton's share of this market, it was estimated that the market potential for PA cotton would be between 17,000 and 27,500 equivalent bales of cotton. The market potential for PA cotton for use as home ironing board covers is estimated to be 2,225 bales.

1820. THE IMPROVEMENT OF SELECTED PHYSICAL PROPERTIES OF PARTIALLY ACETYLATED COTTON FABRICS

Cooper, A. S., Jr.; Cruz, Manuel D.; Murphy, Alton L.; and Cashen, Constance F.

Am. Dyestuff Repr. 48 (20): 43-49. 1959

Partially acetylated (PA) cotton fabrics produced by the usual procedures have reduced resistance to flex abrasion and tearing, which may limit their usefulness in some applications. However, these physical properties can be improved by the addition of fatty acids, higher than lauric, to the acetylating bath; by premercerization; or by addition of softening and lubricating agents. Test results indicate that it is possible by treating to obtain PA cotton products which have greater flex endurance and tear strength after heating for seven days at 160°C. than does untreated PA cotton prior to heating.

1817. HIGH ENERGY  $\gamma$ -IRRADIATION OF VINYL MONOMERS. I. RADIATION POLYMERIZATION OF ACRYLONITRILE

Arthur, Jett C., Jr.; Demint, Robert J.; and Pittman, Robert A.

J. Phys. Chem. 63, 1366-68. 1959

Acrylonitrile monomer, in the presence of water and N,N-dimethylformamide, was exposed to high energy  $\gamma$ -radiation from cobalt-60 and high dose rates ranging from 1.21 to  $5.44 \times 10^{20}$  ev./l./min. Increasing radiation dosage, ranging to  $2.3 \times 10^{24}$  ev./l., increased the intrinsic viscosities of the polymers rapidly and then, at higher dosages, decreased their intrinsic viscosities exponentially. After an inhibition period, which was decreased with increases in the dose rate, the rate of polymerization of acrylonitrile monomer was proportional to the dose rate. In contrast to polymer formation in the presence of water, the polymers formed in N,N-dimethylformamide were completely soluble in



the solvent. This may indicate that polymers formed in the presence of water have a higher molecular weight and are more highly crosslinked than those formed in N,N-dimethylformamide.

1816. MECHANICAL BEHAVIOR OF CYANOETHYLATED COTTON TEXTILES

Conrad, Carl M.

Textile Research J. 29: 287-302. 1959

A rather detailed study has been conducted at the Southern Regional Research Laboratory, as well as at other places, on the textile properties of cyanoethylated cotton. For the most part the studies have been concerned with improvements in rot and heat resistance and a comparison of such improvements with those resulting from acetylation of cotton. In the course of these studies various mechanical properties have been measured. These include breaking strength, knot strength, tearing strength, ultimate elongation, tensile and flexural stiffness, toughness, elastic recovery, wrinkle recovery, and flex and flat abrasion resistance. While many of these data have been published, they are in most cases reported incidentally and with little effort at completeness. The results are expressed in varying units, thus limiting their ready comparison. Finally, they are widely dispersed in many papers, thus not readily accessible. It is the purpose of the present report to assemble the mechanical data on fibers, yarns, and fabrics; to express them in consistent units; and to interpret them in terms of degree of cyanoethyl substitution, conditions of reaction, textile products involved, and fine structure of the fiber. The report also points out the still unexplored areas of chemical substitution, textile product, and conditions of treatment which are in need of further study if an adequate picture of the mechanical behavior of cyanoethylated cotton is to be provided.

1731. PARTIALLY ACETYLATED (PA) COTTON--A STAFF-INDUSTRY REPORT

\*Anderson, Earl V.; and Cooper, Albert S., Jr.

Ind. Eng. Chem. 51, 608-14, 1959

The most important properties of PA cotton are its superior mildew, rot, heat and scorch resistance, compared to untreated material. Cotton is acetylated by reacting cellulose's hydroxyls with acetic anhydride in the presence of perchloric acid. Southern Regional Research Laboratory has developed both a batch and a continuous process to acetylate cotton yarn and fabric. Procter Electric Company is the only American commercial producer of PA cotton and uses the batch process to make material for home ironing board covers. Most promising market for PA cotton is the laundry industry.

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\*Assistant Editor, Industrial and Engineering Chemistry

## 1730. PARTIAL ACETYLATION OF COTTON--COST ANALYSIS APPLICATION

Decossas, K. M.; McMillan, O. J., Jr.; Cooper, A. S., Jr.;  
Koltun, S. P.; Keating, E. J.; and Pollard, E. F.  
Ind. Eng. Chem. 51: 615-18. 1959

This cost analysis shows that costs for partially acetylating cotton vary considerably with variations in annual production and method of processing. For example, the unit manufacturing cost for hypothetical annual production of 34,000 pounds of PA yarn by batch processing is \$1.18, but as production is increased, the unit cost declines rapidly to as low as 19.1 cents per pound of product at an annual production of 4,796,000 pounds. For a comparable production of yarn using continuous operations, the unit manufacturing cost is an estimated 16.4 cents per pound, or 2.7 cents per pound less. For a hypothetical production of 61,500,000 pounds of PA yarn by the continuous method, unit manufacturing costs are estimated to be as low as 14.2 cents per pound of product. For fabric processing lower unit costs from continuous processing would appear to be realized above the capacity of four jigs. Minimum prices were calculated to be as low as 60.9 cents per pound of yarn product and 76.7 cents per pound of fabric product, on the basis of 40% return on fixed capital investment before taxes.

## 1744. HOW MUCH WILL PA COTTON COST?

(Preliminary Study of the Manufacturing and Chemical Costs  
of Partially Acetylating Cotton)

Gardner, H. K., Jr.; Buras, E. M., Jr.; Decossas, K. M.;  
Cooper, A. S., Jr.; Keating, E. J.; and McMillan, O. J.,  
Jr.

Textile Ind. 122 (9): 100-104. 1958

Partially acetylated cotton has outstanding resistance to deterioration by micro-organisms and heat, and has been found to have unusually long service life in various applications such as sandbags, commercial laundry press cloths, household ironing board covers, and water softener bags. This paper gives investment costs, operating expenses, and estimated service charges and break-even points at two profit levels for hypothetical partial acetylation installations. The estimated manufacturing cost for partially acetylating cotton yarn to 15 percent acetyl content in a continuous process, processing about 54 million pounds of scoured yarn annually with reasonable chemical recovery, is reported to be 14.2 cents per pound of product.

1748. PARTIAL ACETYLATION OF COTTON: PRELIMINARY COST STUDIES  
 Gardner, H. K., Jr.; Buras, E. M.; Deccssas, K. M.;  
 Cooper, A. S., Jr.; Keating, E. J.; and McMillan, O. J.,  
 Jr.  
 U. S. Dept. Agr. ARS 72-13: 13 pp. Processed. 1958

Partially acetylated (PA) cotton has outstanding resistance to deterioration by microorganisms and heat, and has been found to have unusually long service life in various applications such as sandbags, commercial laundry press cloths, household ironing board covers, and water-softener bags. This paper gives investment costs, operating expenses, and estimated service changes and break-even points at two profit levels for hypothetical partial acetylation installations. The estimated manufacturing cost for partially acetylating cotton yarn to 15 percent acetyl content in a continuous process, involving processing about 54 million pounds of scoured yarn annually with reasonable chemical recovery, is 14.2 cents per pound of product.

1563. CONTINUOUS CYANOETHYLATION OF COTTON YARNS  
 Janssen, Hermann J.; DuPre', A. Mason; Haydel, Chester H.;  
 Seal, Jeuel F.; and Vix, Henry L. E.  
 Ind. Eng. Chem. 50: 76-79. 1958

A method and apparatus for the continuous cyanoethylation of cotton yarns was investigated. The aim was to avoid excessive losses of reagent to byproduct formation, one of the principal obstacles to the commercialization of the cyanoethylation process. Such losses were considerably reduced, and the products were found to be superior in breaking strength and heat resistance to those cyanoethylated by more conventional procedures.

1753. TOPOCHEMICAL MECHANISMS INVOLVED IN THE PREPARATION AND DEACETYLATION OF PARTIALLY ACETYLATED COTTONS  
 Bailey, August V.; Honold, Edith; and Skau, Evald L.  
 Textile Research J. 28 (10): 861-73. 1958

Iodine sorption and moisture sorption data and some density, x-ray, and infrared data have been obtained on partially acetylated (PA) cotton before and after progressive deacetylation with 2 N hydrochloric acid or with N/2 sodium hydroxide. The results substantiate



the theory that in the partial acetylation of cotton the amorphous regions are acetylated first. They also show that deacetylation of PA cottons by these two reagents proceeds by different mechanisms. With hydrochloric acid, the acetylated amorphous cellulose is deacetylated more or less completely throughout the fiber before the acetylated crystalline is attacked. With sodium hydroxide both are deacetylated simultaneously with little or no selectivity so that deacetylation proceeds annularly from the surface of the fiber inward. The properties of the original PA cottons differed markedly from those of the same acetyl content obtained by deacetylation. The properties depend further upon the reagent used for deacetylation and on the acetyl content before deacetylation. Those differences in properties can be attributed to differences in the proportions and distribution of amorphous, crystalline, acetylated amorphous, and acetylated crystalline cellulose within the fiber and also to differences in the fine structure, degree of lateral order, and stress patterns resulting from the inhomogeneity of the volume changes which take place during acetylation or deacetylation.

1657. IODINE SORPTION VALUES OF SOME CHEMICALLY MODIFIED COTTONS

Bailey, August V.; Honold, Edith; and Skau, Evald L.  
Textile Research J. 28: 895-96. 1958

Some comparative iodine sorption data are reported for partially acetylated, cyanoethylated, and beta-propiolactone-treated cottons. In all cases the iodine sorption capacity increases with the degree of substitution. The results show in general that the iodine sorption values of these chemically modified cottons depend not only upon the substituent and the degree of substitution, but also, in the case of the beta-propiolactone-treated cottons, upon the method of preparation.

1571. HEAT EVOLUTION DURING THE ACETYLATION OF COTTON

Greathouse, Lucien H.; Janssen, Hermann J.; and Haydel, Chester H.

Ind. Eng. Chem. 50: 97-102. 1958

To facilitate control of the process of partial acetylation, reliable information was required on the heat evolved in the reaction of acetic anhydride with cotton cellulose to the extent of one degree of acetyl substitution. To accomplish this it was necessary to eliminate water from the system to avoid heat from the hydrolysis of acetic anhydride. The total amount of heat evolved is uniformly about 106 calories per gram of cotton per degree of substitution, although this is released much more slowly with the raw than with purified cotton. A technique has been proposed for following acetylation by heat evolved and stopping the reaction at a selected point.

1587. SIMPLIFIED CONTROL ANALYSES OF SOLUTIONS USED IN PARTIAL ACETYLA-  
TION OF COTTON

Buras, Edmund M., Jr.; Cooper, Albert S.; and Cruz, Manuel D.  
Anal. Chem. 30: 104-107. 1958

Volumetric methods have been developed for the rapid analysis of acetic acid-acetic anhydride-perchloric acid and acetic acid-water-perchloric acid mixtures which occur in three-component baths during the practical partial acetylation of cotton. Perchloric acid is determined by titration in anhydrous acetic acid solution with standardized potassium biphthalate, using p-naphtholbenzein indicator. Water and acetic anhydride are determined empirically by phase separation in the presence of a large volume of hydrocarbon solvent. The methods are satisfactory as control methods in pilot-scale operations for the partial acetylation of cotton.

1505. PHYSICAL PROPERTIES OF FIBERS AND YARNS OF PARTIALLY ACETYLATED  
COTTONS

Orr, Rollin S.; Weiss, Louis C.; Burgis, Albert W.; and  
Grant, James N.  
Textile Research J. 27: 966-75. 1957

Samples of cotton of Deltapine, Rowden and Stoneville varieties were partially acetylated as bulk cotton and as untreated 14/3 yarns to acetyl contents ranging from 9 to 26%. Breaking loads and elongations at break of single fibers, fiber bundles, and yarns were decreased by the partial acetylation up to about 17%, but showed a tendency to increase above 20% acetyl content. Moisture conditions have less effect on tenacity of yarns of 25% than on those with lower acetyl content. Tenacities of the acetylated yarns when wet were slightly lower, and when desiccator-dried were higher than those of the untreated controls. Below 15%, the relation of density to acetyl content was consistent with calculations based on the preferential reaction of amorphous cellulose in the initial stages of the reaction. Resistance to heat degradation increased with acetyl content up to 25% acetyl. The pH of the water used to rinse the reacted yarns was an important factor influencing heat degradation. Maximum retention of strength occurred when the wash water was in the pH range of 10-11. A slight but consistent difference in heat resistance of the partially acetylated cotton was associated with different varieties.

1494. EXPERIMENTAL YARNS FROM PARTIALLY ACETYLATED COTTON AND BLENDS  
WITH UNTREATED COTTON

Sloan, William G.; Sens, Charles L.; and Buras, Edmund M., Jr.  
Textile Research J. 27: 795-802. 1957

A number of experimental yarns were spun from partially acetylated (PA) cotton stock to determine some of the factors that improve its mechanical processing and yarn properties. These studies indicated that blending PA cotton stock with raw cotton was a better method



of preparation for mechanical processing than the use of an anti-static treatment on the PA stock. Blending resulted in better mechanical processing and improved yarn properties at a lower cost. Blending of high acetyl PA cotton with 40% raw cotton was considered to be the best method of preparation. PA stock prepared from a rain-grown cotton exhibited better mechanical processing characteristics than stock prepared from a longer-staple irrigated cotton. However, yarns spun from the latter type of PA cotton had better properties of strength, elongation, and flex abrasion resistance. The use of a higher twist multiplier in spinning and plying resulted in PA cotton yarns having improved properties of elongation and flex abrasion resistance.

1411. ACID AND ALKALI RESISTANCE OF PARTIALLY ACETYLATED COTTON FABRICS  
Honold, Edith; Keating, Esmond J.; and Skau, Evald L.  
Textile Research J. 27: 400-11. 1957

Investigations have been made of the acid and alkali resistance of partially acetylated cotton fabrics, and it has been found that property changes depend on both the original acetyl percentage and the degree of deacetylation affected by the acid solutions. The effect of hydrochloric acid was studied in greatest detail. High-acetyl fabrics are markedly more resistant to deacetylation than those with low acetyl content. Break- and tear-strength protection against acid solutions increase with the degree of original acetylation. As severity of the acid treatment increases, elongation at break for acetylated fabric increases to a maximum before decreasing below that of the untreated fabric, while elongation at break for the unacetylated fabric decreases in proportion to the loss in breaking strength. Moisture sorption increases rapidly with deacetylation to a maximum value which is successively higher in the order of increasing original acetyl content. Moisture sorptions of the three most highly acetylated fabrics reached and maintained values above that of the unacetylated fabric, suggesting that the structure of the cotton is altered permanently by introduction of more than 15% acetyl. Heat resistance was as great at 11% acetyl as at 28% but acid resistance is markedly greater at the higher acetyl percentages. Less detailed data are presented for other acid solutions, and a few alkaline solutions at two different temperatures.

1419. INFLUENCE OF PRETREATMENT ON THE REACTIVITY OF COTTON AS MEASURED BY ACETYLATION  
Demint, Robert J.; and Hoffpauir, Carroll L.  
Textile Research J. 27: 290-94. 1957

It is apparent from the data presented that differences in the textile form of cotton can have a marked effect on the rate at which it reacts with acetic anhydride in the presence of perchloric acid. Little or no differences in reactivity were observed for the 1-in.

cut silver lap, the raw 3<sup>4</sup>s/2 yarn, and the fabric. The bulkier 7s/3 yarn reacts at a somewhat faster rate, whereas the ground silver shows a definitely lower reactivity than the above group. Pretreatments, such as scouring with low concentrations of sodium hydroxide and alcohol and water extraction were found to increase the reactivity of cotton. Decrystallization also increased the reactivity but not as much as scouring or extraction. However, when decrystallization is followed by solvent exchanging the moisture with acetic acid without drying, the rate of acetylation is materially increased. There are indications that solvent exchange would also supplement the increased reactivity brought about by other pretreatments. Among the simplest and easiest methods of increasing the reactivity of cotton is a treatment with boiling water for a short period.

1423. A PRELIMINARY REPORT ON FULLY ACETYLATED COTTON

Buras, Edmund M., Jr.; Hobart, Stanley R.; Hamalainen, Carl;  
and Cooper, Albert S., Jr.

Textile Research J. 27: 214-22. 1957

A small-scale method is reported for preparing a completely, or almost completely substituted cellulosic product known as fully acetylated (FA) cotton from cotton raw stock, yarn, or fabric by the application of acetic anhydride and perchloric acid catalyst in a diluent which minimizes the tendency of the product to dissolve. Its general properties and behavior in laboratory tests show it to have some properties in which it is superior to previously known cellulosic fibers, including partial acetates and triacetates. FA cotton has good tenacity, both wet and dry, and flex-abrasion endurance; it has some thermoplasticity, yet shows no sticking at ironing temperatures below 250°C.; it has low moisture regain and is dyeable with ordinary acetate colors. Work in progress indicates that treatment of yarn and fabric may be carried out satisfactorily in commercial type stainless steel equipment.

1424. PROTECTIVE TREATMENTS FOR COTTON AWNINGS

Brysson, Ralph J.; Berard, W. Norbert; and Bailey, John V.

Textile Research J. 27: 209-13. 1957

The cooperative research program of the USDA's Southern Utilization Research Branch and the National Canvas Goods Manufacturers' Association for improvement in the durability of cotton awnings and other outdoor fabrics is described, and results of the preliminary weathering exposure studies performed under the joint program are presented. Data were obtained on a number of laboratory experimental and proprietary weather-resistant treatments for awning fabrics that had been exposed to outdoor weathering. Laboratory-prepared coatings and standard commercial coatings are compared after twelve months' weather exposure. Data are presented to demonstrate the increase in weather durability of heavy duty cotton sewing threads treated by the vat dyeing and acetylation process.



14.

1429. THE CELLULOSE-ALKALI HYDROXIDE-WATER SYSTEM IN THE CYANOETHYLATION OF COTTON CELLULOSE

Klein, Elias; Weaver, J. W.; Webre, Beverly G.; and Jurgens, Julian F.

Textile Research J. 27: 50-53. 1957

When cotton cellulose is cyanoethylated with a large excess of acrylonitrile in the presence of aqueous alkali hydroxides at a fixed time and temperature, the rate of reaction is controlled by the ratios of base : cellulose : water. The variations in yield and rate of cyanoethylation can be explained by considering the changes brought about in cellulose ion concentration, solubility of acrylonitrile, and bond strengths, by varying the amount, concentration and nature of the alkali hydroxide on the cellulose. The microbiological resistance of the product is dependent on the same ratios because of the formation of carboxyl groups in the product, the rate of which formation is governed by the strength and quantity of the aqueous base and the time of the reaction.

1418. THE INFLUENCE OF MICRONAIRE FINENESS AND PRIOR TREATMENTS ON THE CYANOETHYLATION OF COTTON

Reinhardt, Robert M.; and Tallant, John D.

Textile Research J. 27: 24-29. 1957

Fiber fineness, as measured by the Micronaire, and prior treatments have been found to be important factors in determining the rate and extent of cyanoethylation of cotton. Fineness was found to be a good index of the rate of reaction for both raw and pressure-boiled cotton fibers. Prior treatment of yarn by ethanol extraction, pressure boiling with 2% caustic, ethanalamine extraction, and mercerization, both slack and at constant length, affected the rate of cyanoethylation and the rot resistance of the product.

1431. MICROSCOPICAL OBSERVATIONS ON PARTIALLY ACETYLATED COTTONS AND RELATED FIBERS

Tripp, Verne W.; Giuffria, Ruth; and deGruy, Ines V.

Textile Research J. 27: 14-24. 1957

Effects of acetylation on the morphology and submicroscopic structure of cotton have been studied by light and electron microscopy. The cross sectional areas of partially acetylated (PA) fibers increase with degree of substitution; the average refractive index decreases with increase in acetyl content, as to the indices measured parallel and perpendicular to the fiber axis. Refractive index measurement appears to be a feasible method for estimating the chemical composition of PA cotton. At early stages of esterification, unevenness of reaction along the length of fibers may be demonstrated by dyeing and swelling techniques. Acetylation causes the surface of cotton to become smoother, and obliterates the microfibrillate pattern characteristic of scoured fibers. PA



cotton fibers swell when embedded in methacrylic esters by polymerization. Separation of the lamellae of the secondary wall permits electron microscopical observations on the interior elements of the fiber to be made on this cross section of the specimen. The results of microscopical examination are considered in terms of fiber structure.

1446. HYDROLYSIS OF ACETIC ANHYDRIDE IN CONCENTRATED ACETIC ACID WITHOUT CATALYSIS

Janssen, H. J.; Haydel, C. H.; and Greathouse, L. H.  
Ind. Eng. Chem. 49: 197-201. 1957

The uncatalyzed hydrolysis of acetic anhydride in concentrated acetic acid solution has been followed by thermometric methods, based on observations that the heat evolved during reaction, when catalyzed with perchloric acid, is an accurate measure of the quantities reacting. The initial reaction is followed by direct measurement of temperature rise, which had a negligible effect on the hydrolysis rate for the first hour. In the second procedure aliquots from a reacting mixture held at constant temperature are analyzed by observing the temperature rise when perchloric acid is added. The reaction, for the nearly equivalent concentrations of water and anhydride employed, appears to be of the second order, with a rate coefficient of approximately  $6.5 \times 10^{-4}$  at 25°C. This agrees with literature values. The effect of the dicyandiamide treatment on cyanoethylated cotton, partially acetylated cotton, and aminized cotton, as well as an acetate and viscose rayon, is also discussed. Treatment with dicyandiamide is not stable after washing in water.

1506. SOLUBILITY OF ACRYLONITRILE IN AQUEOUS BASES AND ALKALI SALTS

Klein, Elias; Weaver, J. W.; and Webre, Beverly G.  
Chem. & Eng. Data Ser. 2: 72-75. 1957

The solubility of acrylonitrile has been measured in various concentrations of lithium, sodium and potassium hydroxides. The addition of hydrotropic salts, such as sodium iodide, sodium benzoate, sodium xylene sulfonate, and potassium iodide, increases the solubility of acrylonitrile in water and in aqueous base solutions. The hydrotropic effect of these salts in aqueous base solutions ceases at specific concentrations of the base; these concentrations are dependent on the nature of the hydrotropic salts and of the bases. In general, the greater the hydrotropic effect of the salt in water, the greater will be the range of base concentrations over which the effect will prevail.

## 1511. VAPOR PHASE METHOD FOR PREPARATION OF POLYACRYLONITRILE COATED COTTON YARN AND PHYSICAL PROPERTIES OF THE PRODUCT

Haydel, Chester H.; Janssen, Hermann, Jr.; Seal, Jeuel F.;  
Vix, Henry L. E.; and Gastrock, Edward A.  
Textile Research J. 27: 975-82. 1957

Acrylonitrile vapors were polymerized within and upon the individual fiber surfaces of scoured cotton yarns to yield coated products having new and interesting properties. The uniformity of the polyacrylonitrile coating is shown in electron micrographs of the fiber surfaces. Breaking strengths were increased appreciably, particularly when the process was applied to prestretched yarns. High frictional characteristics were exhibited when one coated yarn was pulled against another. Excellent resistance to rot and flat abrasion was obtained in conjunction with a relatively minor improvement in resistance to acid degradation. No essential change in heat and weather resistance was noted. Resistance to flexing, however, was adversely affected by the presence of the polyacrylonitrile. These polymer coated yarns can be prepared with essentially the same equipment and procedures as required for the vapor phase cyanoethylation of cotton; the only exception is that a different catalyst is employed. This illustrates the utility of acrylonitrile for preparation of a variety of useful cotton products.

## 1344. CYANOETHYLATION OF COTTON FABRIC

Greathouse, L. H.; Janssen, H. J.; Berard, W. N.; and  
Haydel, C. H.  
Ind. Eng. Chem. 48: 1263-67. 1956

A pilot-plant study was undertaken to determine the conditions affecting uniformity of treatment in the cyanoethylation of cotton yarns and fabrics. Results indicate that local overheating during the reaction is one of the principal causes of uneven treatment. By careful control of reaction conditions, 45-yard lengths of standard print cloth were cyanoethylated within limits of 0.40 to 0.42 cyanoethyl addition per anhydroglucose unit. This evenness of modification existed even between single yarns and fibers and along the length of individual fibers. Special pilot-plant equipment was adapted to provide the required conditions, and is described.

## 1358. PHYSICAL PROPERTIES OF CHEMICALLY MODIFIED COTTONS. PART II: EFFECTS OF PARTIAL ACETYLATION

McDonald, A. W.; Humphreys, Geraldine C.; Orr, R. S.;  
and Grant, J. N.  
Textile Research J. 26: 646-52. 1956

Yarns manufactured from samples of the same six cotton varieties discussed in the previous paper were partially acetylated to an acetyl content of approximately 25% while held under tension. Certain physical properties of the component fibers, fiber bundles, and yarns were then measured. The changes in most properties were found to be associated with differences in the cottons and the acetyl contents. The averages for breaking loads and tenacities of the fibers were decreased while their linear densities and secant moduli were increased. Breaking loads, linear densities, and secant moduli of the yarns were increased. Elongation of the yarns at break was decreased, while tenacity remained essentially unchanged. The changes were greater for some cottons than for others; whether the changes were advantageous or disadvantageous would depend somewhat upon the use to which acetylated cotton is to be put.

## 1356. PARTIALLY ACETYLATED COTTON FIBER AND TREATMENTS TO FACILITATE PROCESSING INTO YARN

Sloan, W. G.; Buras, E. M., Jr.; Goldthwait, C. F.; and  
Murphy, A. L.  
Am. Dyestuff Reprtr. 45: 429-33. 1956

A study has been made of partially acetylated cotton stock and treatments applied to facilitate processing into yarn. Changes in physical properties of the fiber upon acetylation are discussed and difficulties encountered in mechanical processing are described. The investigation of possible methods of



overcoming these difficulties, both by the application of antistatic finishes and by spinning blends of small amounts of raw cotton with acetylated cotton, is described. Data are given on strength and heat endurance of yarns spun from small lots of acetylated stock and the results of both the antistatic treatment and the blending upon these properties are shown.

1262. CERTAIN PHYSICAL PROPERTIES OF SELECTED SAMPLES OF CHEMICALLY MODIFIED COTTONS

Grant, J. N.

Textile Research J. 26: 74-80. 1956. (Republished, The Textile J. of Australia 31: 550-56. 1956)

Measurements are given on certain physical properties of fibers and yarns for cottons which were chemically modified by mercerization, ethylamine decrystallization, aminization, carboxymethylation, acetylation, and cyanoethylation. The changes in physical properties are shown to be affected by the type of modifications, the extent of reaction, and the tensional forces on the yarns during the treatment. A spread in the percent changes was found when untreated cottons with their natural noncellulosic constituents were chemically treated under controlled conditions.

1295. THERMOMETRIC DETERMINATIONS OF WATER AND ACETIC ANHYDRIDE IN ACETIC ACID

Greathouse, L. H.; Janssen, H. J.; and Haydel, C. H.  
Anal. Chem. 28: 357-61. 1956

The temperature rise occurring during the exothermic reaction of water and acetic anhydride in glacial acetic acid solution, catalyzed by a trace of perchloric acid, is employed to determine the concentration of either of these reactants in the presence of an excess of the other. Two different techniques are described. In one, the reaction is conducted in a Dewar flask. The temperature rise which takes place is a direct measure of the component being determined. By the other procedure either water or the anhydride is titrated in glacial acetic acid solution with a standard solution of the other until no further temperature rise occurs. Either procedure is conducted with adequate protection from atmospheric moisture. A qualitative method is described to detect the presence of water, acetic anhydride, or perchloric acid, within limits, in glacial acetic acid solution.

1355. NEW TEXTILE PRODUCTS FROM COTTON--PARTIALLY ACETYLATED COTTON

Buras, E. M., Jr.; and Persell, R. M.

U. S. Dept. Agr. ARS 72-4, 24 pp. Processed 1956

This brochure summarizes information on PA (partially acetylated) cotton. Topics include: fibrous cellulose derivatives

from cotton; chemical nature of PA cotton; its properties, present and potential uses, availability, and estimated costs. Information on additional textile products from cotton, and cotton as a raw material for the chemical industry, is summarized, and a bibliography of 22 titles is included.

1347. EFFECT OF ALKALINE HYDROLYSIS ON THE PROPERTIES OF CYANOETHYLATED COTTON

Mazzeno, L. W., Jr.; Reinhardt, R. M.; Reid, J. D. and Dickson, J. B.

Textile Research J. 26: 598-606. 1956

Cyanoethylated cotton has been subjected to treatment with excess 1% aqueous sodium hydroxide at temperatures of 22°, 60°, and 97°C. Rates of cleavage of cyanoethyl groups at these temperatures have been determined. Resistance to rotting is destroyed by removal of part of the cyanoethyl groups. Heat resistance is decreased by the alkaline treatment, but only to the extent that nitrogen is removed. It appears that heat resistance is directly proportional to the nitrogen content regardless of the previous history of the sample. Dyeing characteristics, measured by a differential staining technique, show reversion to the color of untreated cotton even though only half the nitrogen is removed. Physical properties are not adversely affected by alkaline hydrolysis. Tenacity increases as groups are cleaved but does not return to the original value of the gray yarn. This is the usual case with other cellulose derivatives. The knot strength data do not indicate brittleness. Hydrolysis has little effect on elongation.

1342. THE CELLULOSE-SODIUM HYDROXIDE-WATER SYSTEM IN THE CYANOETHYLATION OF COTTON CELLULOSE

Weaver, J. W.; Klein, Elias; Webre, Beverly G.; and Dupre', Elsie F.

Textile Research J. 26: 518-23. 1956

When cotton is cyanoethylated with a large excess of acrylonitrile in the presence of aqueous alkali at fixed time and temperature, the extent of cyanoethylation and byproduct formation is controlled by the ratios of cellulose, sodium hydroxide and water employed. The mechanical restraints offered by the yarn and fabric structures alter these optimum conditions as well as the extent of cyanoethylation which takes place. Cyanoethylated cottons, having essentially equal nitrogen contents but different properties, can be prepared from a large number of compositions of cellulose, sodium hydroxide and water. High sodium hydroxide contents in the starting mixtures result in substantial conversion to carboxyethyl groups with a subsequent loss of resistance to microbiological attack.



1265. THE EFFECT OF LAUNDERING, MERCERIZING AND SIMULATED VAT DYEING ON THE PROPERTIES OF PARTIALLY CYANOETHYLATED COTTON

Reinhardt, R. M.; Markezich, A. R.; Moore, H. B.; and Reid, J. D.

Textile Research J. 26: 423-29. 1956

Cotton sheeting cyanoethylated to various nitrogen contents, from 2.2 to 6.4%, was subjected to laundering, mercerizing, or simulated vat dyeing. The samples were then analyzed for thread count, weight, and thickness and tested for breaking strength, elongation, tearing strength, abrasion resistance, air permeability, stiffness, moisture regain, heat resistance, and rot resistance. In addition, wrinkle recovery of the partially cyanoethylated and untreated cloth was determined. Results indicate that neither laundering, mercerizing nor simulated vat dyeing seriously affects the usual textile properties of partially cyanoethylated cotton. The rot- and heat-resistance of samples of more than 4% nitrogen content was not greatly impaired by these treatments; however, a sample of 3.2% N. was not rot-resistant after these subsequent treatments.

1268. INFLUENCE OF MOISTURE SORPTION AND OTHER PRETREATMENTS ON THE ACETYLATION OF COTTON WITH ACETIC ANHYDRIDE AND PYRIDINE

Blouin, F. A.; Reeves, R. E.; and Hoffpauir, C. L.

Textile Research J. 26: 272-75. 1956

A study of the acetic anhydride-pyridine procedure for acetylation of cotton has shown that the degree of acetylation under specified conditions is not only dependent on the moisture content but also on the previous moisture sorption history of the sample. The data indicate markedly greater reactivity under the conditions employed of cotton fibers which are desorbing moisture over those of the same moisture content which are absorbing moisture. The effect can be obscured by long pretreatment with pyridine. Increased reactivity similar to that produced by moisture can be obtained by using a number of other pretreatments. However, the degree of reactivity produced by high moisture contents could be exceeded only with pretreating agents generally considered to penetrate the crystalline regions of the cotton. It was also found that the increased reactivity produced by treatment with strong alkali was not completely lost on drying.

1266. THE EFFECT OF PARTIAL ACETYLATION ON THE PORE-SIZE DISTRIBUTION OF COTTON FABRICS

Honold, E.; Boucher, R. E.; and Skau, E. L.

Textile Research J. 26: 263-71. 1956

Partial acetylation increases the weight and decreases the density of a cotton fiber and, as acetylation increases, the coarseness of the fiber increases rapidly. When acetylation is carried out on either yarns or fabrics, the geometric structure of the sample changes so that the yarns become tighter and the fabrics denser

according to the restriction placed on the enlarged fibers. In order to gain some insight into the structural modification of a fabric after partial acetylation, the pore-size distribution of the void volumes within the fabric boundaries were determined on a cotton-sheeting series, whose acetyl content ranged from 0.0% to 28.2%. As the acetyl content of the sheeting samples increased, there was a general downward trend in total void volume within the interfiber region. Further analysis of the interfiber (intra-yarn) void volumes by means of pore-sizing distribution curves showed a shift of the whole curve toward a smaller pore-radius position as acetylation increased up to 14.6%. At higher acetyl contents the predominant pore size (peak position) remained approximately the same, but there was a diminution in volume at each pore-radius position throughout the greater portion of the interfiber and interyarn pore-size ranges. A photomicrograph of the yarn cross section of the most highly acetylated sample (28.2% acetyl) revealed that the fibers had become considerably distorted as they increased in coarseness within the confined spaces of the constricted yarn. For comparison, this study included two additional fabrics whose constructions were as nearly alike as possible and whose yarns had been spun, respectively, from Iquitos cotton and from Iquitos fibers after partial acetylation in the fiber form to 17.4% acetyl. The peak shift from the unacetylated to the acetylated was in the same direction and of the same order of magnitude as that for the two comparable members of the sheeting series.

#### 1267. IMPROVED WEATHER RESISTANCE BY ACETYLATED VAT-DYED COTTON

Berard, W. N.; Gremillion, S. G., Jr.; and Goldthwait, C. F.  
Textile Research J. 26: 81-86. 1956

Cotton has been made unusually resistant to degradation by weather by first dyeing it with certain light-scale vat dyes and following this with partial acetylation. Vat-dyeing alone or partial acetylation alone do not make cotton significantly more resistant to deterioration by sunlight than undyed fabrics, except for a few colors which do have a protective effect. However, when these two processes are combined, excellent resistance to solar radiation is added to the excellent mildew- and rot-resistance of partially acetylated cotton. Data were obtained on a number of individual vat-dyed and vat-dyed and acetylated cotton materials that had been exposed to outdoor weathering. From the results of these tests, it is estimated that the combination of vat dyeing with light-fast colors and acetylating may more than double the outdoor service life compared to cotton vat dyed only, or acetylated only, with somewhat better color retention when the cotton has been both dyed and acetylated.



1195. DETERMINATION OF BETA, BETA'-OXYDIPROPIONITRILE AND ETHYLENE CYANOHYDRIN WITH ACRYLONITRILE BY INFRARED ABSORPTION

DuPre', E. F.; Armstrong, A. C.; Klein, Elias; and O'Connor, R. T.

Anal. Chem. 27: 1878-79. 1955

This paper presents an analytical method for the determination of beta, beta'-oxydipropionitrile and ethylene cyanohydrin in admixture with acrylonitrile. In several reactions involving acrylonitrile the efficiency is decreased by the formation of byproducts among which are beta, beta'-oxydipropionitrile and ethylene cyanohydrin. Studies of the effect of catalyst, temperature, etc., to reduce the formation of these undesirable byproducts require a method for their analysis in admixture with acrylonitrile. A simple multicomponent analysis by means of infrared absorption spectra is described which permits a simultaneous determination of the three compounds.

1194. DENSITY OF MODIFIED COTTONS DETERMINED WITH A GRADIENT COLUMN

Orr, R. S.; Weiss, L. C.; Moore, H. B.; and Grant, J. N.

Textile Research J. 25: 592-600. 1955

A rapid method for measuring the density of cellulosic materials with a gradient column is described. Accuracy of the method compares favorably with slower ones. Densities of several cottons before and after chemical modification by partial acetylation, carboxymethylation, aminization, and mercerization are given. Percent acetyl can be expressed as a function of density in a linear empirical equation over a range of 13 to 42% acetyl with a precision of  $\pm 2\%$ . Density measurements of decrystallized, ball-mill ground and acid-hydrolyzed cottons were in agreement with the generally accepted concept of the crystalline-amorphous cellulose phase composition of these materials. Cottons from which water was removed by solvent exchange was found to have a high density before, and a low density after, air drying.

1132. PREPARATION OF PARTIALLY CYANOETHYLATED COTTON WITH ACRYLONITRILE

Daul, G. C.; Reinhardt, R. M.; and Reid, J. D.

Textile Research J. 25: 246-53. 1955

The preparation of partially cyanoethylated cotton with acrylonitrile in the presence of sodium hydroxide is described, including effects of changes in time, temperature, and concentration of reagents. Products with retention of the fibrous form have been obtained with degrees of substitution up to 2.7 cyanoethyl groups per anhydroglucose unit. Hydrolysis of the cyanoethyl group occurs readily under alkaline conditions and results in both cleavage and conversion to the carboxyethyl groups. Maximum conversion in the latter case was 29%.



## 1133. PROGRESS REPORT ON CYANOETHYLATED COTTON

Grant, J. N.; Greathouse, L. H.; Reid, J. D.; and Weaver, J. W.  
Textile Research J. 25: 76-83. 1955

The mechanism of cyanoethylation of cotton is discussed, and it is shown that for best efficiency the pickup of sodium hydroxide must not exceed 15% of the weight of the cotton. Increases in the breaking strength or elongation of yarns are results of changes in frictional forces. Physical properties of cyanoethylated fabrics reflect the properties of the yarn and are also dependent on fabric construction. Extremely high resistance to flat abrasion is obtained with high cyanoethyl substitution. The density of cyanoethylated cotton is shown to be linearly related to nitrogen content, and the spread of values to give an estimate of uniformity of treatment. Cyanoethylated cotton can be dyed by methods developed for polyacrylonitrile fibers such as those employing acid dyes in the presence of cuprous ion, and the dyed samples so produced are suitable for cross sectioning for microscopic examination. The intensity of dye color can be used as a measure of the amount of cyanoethylation.

## 1200. PARTIAL ACETYLATION OF PAPER FOR CHROMATOGRAPHY

Buras, E. M., Jr.; and Hobart, S. R.  
Anal. Chem. 27: 1507-8. 1955

Reference is made to the use of paper that is less hydrophilic than ordinary filter paper in specialized applications of paper chromatography. Acetylated filter paper has been used as the carrier for the stationary phase in some chromatographic separation procedures. This paper described a relatively rapid laboratory method for partial acetylation of filter paper to give a strong, white product.

## 1080. THE DYEING OF CYANOETHYLATED COTTON

Schuyten, H. A.; and Weaver, J. W.

Textile Research J. 24: 1005. 1954

Methods employed in the dyeing of polyacrylonitrile fibers can be applied to cyanoethylated cotton of low substitution; and basic dyes that do not ordinarily dye cotton will dye cyanoethylated cotton. Acid dyes only slightly discolor untreated cotton, which is increased to an extremely light shade by the presence of cyanoethyl groups. The dyes are absorbed to only a negligible extent by cyanoethylated cotton with substitutions as high as 1 cyanoethyl group per anhydroglucose unit (6.5% N).

## 1079. RESISTANCE TO PARTIALLY ACETYLATED COTTON FABRIC TO NITROGEN DIOXIDE AND TO HYDROGEN CHLORIDE

Schrieber, W. T.; Bullock, A. L.; and Ward, W. L.

Textile Research J. 24: 819-22. 1954

The resistance of partially acetylated cotton to the tendering action of nitrogen dioxide is of interest because of the possible use of partially acetylated cotton filters for removing dusts from fume-laden air or for other purposes where resistance to oxidizing agents or to acids is required. A possible explanation of the protective effect of partial acetylation is that by substituting acetyl groups for the more accessible of the hydroxyl groups, these larger groups interfere with access of the gas to vulnerable groupings in the cellulose molecule. The protective action of acetylation against breaking of the cellulose chains is probably due to blocking of hydrolysis of the glucosidic linkages.

## 1078.1 THE EFFECT OF TIME AND TEMPERATURE OF PRESOAKING AND THE TEMPERATURE OF ACETYLATION ON THE RATE AND DEGREE OF ACETYLATION OF COTTON FIBERS

Taylor, James L; and Owens, Emmet Dennis.

Contractor: A. French Textile School, Georgia Institute of Technology, Atlanta, GeorgiaTextile Research J. 24: 810-19. 1954

In a study of the effects of time and temperature of presoaking on the rate of acetylation of cotton fibers, it was found that as the temperature of the glacial acetic acid used for presoaking increased, the degree of acetylation increased rapidly, particularly for the shorter presoaking periods. As the presoaking time increased, however, the temperature had less effect in most cases. Six varieties of cotton were used in the investigations. The order of maximum acetyl content under the same acetylating conditions obtained for the various fibers was Memphis, Acala 1517, Stoneville 2B, Empire Bale, Bob Shaw, and Lockett 140. It was found also that the more mature the fiber, the less the degree of acetylation under constant conditions, generally speaking. The higher

temperatures of acetylation produced greater degrees of acetylation, the fibers also suffered greater degradation; an increase of 58°F. to 82°F. approximately doubled the acetyl content obtained, weakening was so great that fiber strengths were unobtainable at 82°F.

996. PRACTICAL PARTIAL ACETYLATION OF COTTON

Buras, E. M., Jr.; Cooper, A. S.; Keating, E. J.; and Goldthwait, C. F.

Am. Dyestuff Repr. 43: 203-08. 1954

Practical processes for the partial acetylation of cotton, well adapted for commercial use, have been worked out. The process converts cotton into a new type of textile fiber with several new or improved properties. Several commercial developments are based on these processes. Fabric can be acetylated on stainless steel dye jigs, as used in cotton finishing plants, or on a newly developed continuous range; yarns, in package form or continuously as warp; raw stock, in a raw stock dyeing machine. The processes employ acetic acid and anhydride, with small amounts of perchloric acid as catalyst. Data on the concentration of chemicals used, duration of treatments, temperature, and other conditions required for best results have been determined.

850. IMPROVEMENT OF COTTON CLOTH IN RESISTANCE TO SOILING AND IN EASE OF WASHING

Utermohlen, William P., Jr.; Ryan, Mary E.; and Young, Doris O.  
Contractor: Institute of Textile Technology, Charlottesville, Va.

Textile Research J. 21: 510-21. 1951. Republished: Textile J. Australia 26: 1115-18, 1120, 1122-23. 1952

The general problem of producing resistance to soiling in cotton textiles is presented, and the effects of a number of treatments upon the ease of soil acquisition by cotton cloth and upon the ease of soil removal from the soiled cloth by washing are described. Of the treatments employed, those which altered the electrical change upon the cloth by introducing acidic groups appeared to have the most favorable general effect in increasing soiling-resistance and ease of soil removal. A partial-acetylation treatment was noticeably effective in increasing resistance to dry soiling.

517. IMPROVEMENT OF THE RESISTANCE OF COTTON CLOTH TO SOILING

Utermohlen, William P., Jr.

Contractor: Institute of Textile Technology, Charlottesville, Va.

Am. Dyestuff Repr. 39: 262-64. 1950

The effect of a number of treatments upon the ease of soil acquisition by cotton cloth and upon the ease of soil removal from the



cloth by washing has been studied. Among the treatments employed were the following: various amounts of moisture; various amounts of starch; cationic and anionic softening agents; durable and non-durable hydrophobic finishes; prepolymerized vinyl-emulsion polymers; ureaformaldehyde condensates polymerized in the cloth; and several treatments, such as partial acetylation, producing chemical alterations in the cotton cellulose. Cloths so treated were soiled with several kinds of pigment, from liquid dispersions or in a dry state, and washed. Effects of these treatments upon the ease of soiling and of soil removal are presented and briefly discussed. Those which alter the electrical charge upon the cloth by introducing acidic groups appeared to have the most favorable general effect in increasing soil resistance and ease of soil removal. Partial acetylation was particularly effective in increasing resistance to dry soiling.

#### 800. PHYSICAL PROPERTIES OF CHEMICALLY MODIFIED COTTONS

Grant, J. N.

The Cotton Research Clinic 1952: 55-57

The effect of chemical modification on the physical properties of fibers and yarns was studied through tests on 6 cotton from commercial production, representing a broad range in physical characteristics. Samples of SxP, Acala 1517, Stoneville 2B, Coker 100 Wilt, Deltapine, and Rowden 41B, were processed into yarns of 16/2 construction, and 60-yard skeins were acetylated, mercerized, carboxymethylated, decrystallized, and aminized. From measurements of length, breaking load, weight per unit length, and elongation-at-break of yarns and individual fibers taken from the yarns, the tenacity and stress-strain ratio-at-break were calculated. Fiber tenacity by the flat-bundle method also was determined.

#### 702. HEAT-RESISTANCE OF PARTIALLY ACETYLATED COTTON FABRICS

Honold, Edith; Poynot, Janice; and Cucullu, Alva F.

Textile Research J. 22: 25-29. 1952

Specimens of commercial sheeting--unacetylated and acetylated (17.4%, 23.4% and 28.7% acetyl)--were heated at 160°C. (320°F), in dry, oxygen-free nitrogen, in dry air, in water vapor, and in a mixture of water vapor and air for varying periods of time. In nitrogen, the loss of breaking strength by acetylated fabrics was less than 3%, in air it was 4-7%, in water vapor 4-8%, and in air and water vapor mixture, 8-16%, in comparison with losses for the unacetylated controls of 24%, 46%, 82%, and 83%. Losses in elongation at break tended to parallel losses in breaking strength. No measurable quantity of acetyl was lost from the acetylated fabrics during heating. After heating and reconditioning, all the fabrics showed a slight decrease in weight and in percentage of moisture regain, and a slight increase in thickness.

## 713. PARTIAL ACETYLATION OF COTTON

Cooper, Albert S.; Voorhies, Samuel T., Jr.; Buras, Edmund M., Jr.; and Goldthwait, Charles F.  
Textile Ind. 116 (1): 97-102, 194-95. 1952

Processes are described for partially acetylating a yard or two of cotton cloth at a time, or small amounts of raw stock or loose yarn on a laboratory apparatus; for treating 50-lb. lots of raw stock in a small stainless steel kier, and treating singles and other low-twist yarns, thread, twine, cord, net, and raw stock on a 6-lb. dyeing machine; and for treating fabric on a dye jig. A dyeing test is used to determine qualitatively the uniformity of the treatment within a sample of any desired size. The cost of acetylating is probably, on a weight basis, about half the cost of the average gray goods.

## 629. CHEMICAL SUBSTITUTION IN FIBROUS COTTON AND RESISTANCE OF SUBSTITUTED COTTON TO MICROBIOLOGICAL DETERIORATION

Goldthwait, Charles F.; Buras, Edmund M., Jr.; and Cooper, Albert S.  
Textile Research J. 21: 831-40. 1951

The resistance for months to deterioration by microorganisms (in soil burial) of suitable acetylated fibrous cottons, some with only one-third of the hydroxyl groups substituted, depends upon the distribution, as well as upon the total number of the acetyl groups present. At one-third substitution the amorphous cellulose is converted to triacetate; the cotton fiber still contains about two-thirds of the original cellulose, which is present as crystalline material surrounded by acetylated cellulose. The swelling capacity of the cotton in water is greatly reduced. Attacks by microorganisms apparently begin at the most readily accessible amorphous cellulose. Protection by partial acetylation is believed to be due to the blocking of hydroxyl groups, the filling of spaces between chains in the amorphous cellulose, and the suppression of swelling.

## 570. ACETYLATION TO MAKE A NEW TEXTILE

Goldthwait, Charles F.  
Yearbook of Agr., (U. S. Dept. Agr.) 1950-51. 421.-26.

The processes used at the Southern Regional Research Laboratory to produce partially acetylated cotton, cellulose acetate, or cotton in which some of the hydroxyl groups have been replaced by acetyl groups, are described in detail. The improved properties, including mainly the better rot resistance, of the virtually new cotton product are discussed. For example, partially acetylated cotton bags of the type used in household water-softening systems last several times as long as untreated bags.



## 381. PARTIAL ACETYLATION OF COTTON CELLULOSE BY KETENE

Hamalainen, Carl; and Reid, J. David  
Ind. Eng. Chem. 41: 1018-21. 1949

Linters and cotton sewing thread have been acetylated with ketene. Treatment involves preswelling with water, removal of excess water by extraction, suspension of the cotton in an inert solvent containing a catalyst, and treatment with ketene as prepared by pyrolysis of acetone. Samples containing up to 17% acetyl retained their fibrous structure with only slight degradation. The ketene acetylation was accompanied by an objectionable polymerization of ketene which produced a yellow to dark brown coloration of the sample. The color could be removed by hot alcohol. Although the emphasis was on the reaction of water-activated, solvent-dehydrated cellulose with ketene, some experiments were tried in which the cotton was swollen with acetic acid before the introduction of the ketene. The acetylation was probably due to the acetic anhydride formed.

## 184. ACETYLATED COTTON HIGHLY RESISTANT TO ROTTING

Goldthwait, Charles F.; McLaren, James; and Voorhies, S. T., Jr.  
Textile World 96: 115-17, 212, 216. 1946

Partial acetylation of cotton cellulose in the form of fiber, yarn, thread, or cloth can be so conducted that the cotton retains its outward appearance but is highly mildew- and rot-resistant, and more resistant to heat than ordinary cotton, has a lower moisture regain, and dyes similarly to acetate rayon. The partial acetylation was performed in various ways; for example, yarn and thread were treated in a stainless-steel package yarn-dyeing machine, while for cloth a series of laboratory-size paddlers, aging chambers, and washers were used. Successful acetylations up to 30% acetyl content are reported. Processing cost is discussed and various uses are suggested. Rotting and outdoor exposure tests reported indicate the high degree of resistance to microbial attack imparted by the treatment.

PATENTS**CHEMICALLY MODIFIED TEXTILES**

U. S. Pat. No. 2,971,815, February 14, 1961  
Bullock, Austin L.; and Guthrie, John D.

A process for producing the partial ethers of the partial esters of cellulose. This process is characterized by the ability to achieve a high degree of chemical modification with the retention of desirable fabric properties. The process involves crosslinking of the cellulose with a polyfunctional reagent prior to or concurrent with the chemical modification.

**1558. PARTIAL ACETYLATION OF COTTON FIBERS**

U.S. Pat. No. 2,816,003, Dec 10, 1957  
Keating, Esmond J.; Cooper, Albert S., Jr.; and Buras  
Edmund M., Jr.

A process for the partial acetylation of cotton fibers. Cotton fibers are acetylated to a degree of substitution of from 0.5 to 2.0. Heat and rot resistance is improved thereby.

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